PATENT SPECIFICATION

NO DRAWINGS

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1,108,811

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Date of filing Complete Specification (under Section 3 (3) of the Patents Act 1949): 13 July, 1965.

Application Date: 12 May, 1964. *No. 19737/64.*

Application Date: 12 May, 1964. *No. 19738/64.*

Application Date: 18 March, 1965. *No. 11566/65.*

Complete Specification Published: 3 April, 1968.

Index at acceptance:—**D1** P(A1, A6, A12, A18, A19, AX, B2A1, B2A2, B2B1, B3, B4D, B5A, B5B, B5C, C2A2C, C2A10, C2A12A1, C2A12A4, C2A12A5, C2A12A7, C2A12A10, C2A12B5, C2C1, C2C2, C2C3, C2C5, C2C7, C2C8, C2C9, C2C10, C2C11, C2C18, C2CX); **C3** R(22C6X, 22C8R, 22C10, 22C11, 22C12, 22C13M, 22C13S, 22C16, 22C25, 22C28X, 22D1A2, 22D1A3, 22D1AX, 22D2AX, 22D2BX, 22D3B, 22D3D1, 22D3DX, 22L1B, 22L6H)

Int. Cl.:—**D 06 m 15/60**

COMPLETE SPECIFICATION

Treatment of Shaped Articles

We IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the treatment of shaped articles, particularly textile materials and films, with certain polyamide condensates.

We have found that the products obtained by the condensation of dicarboxylic acids with a mixture of a diaminopolyalkyleneoxy compound with either an aliphatic, cycloaliphatic or aromatic diamine or with an aliphatic, cycloaliphatic or alkylcycloaliphatic amino acid and/or lactam or with both are useful for the treatment of shaped articles in order to impart valuable properties. The shaped articles may be composed of either natural or synthetic polymeric material.

Thus the invention provides a process for the treatment of shaped articles composed of natural or synthetic polymeric material which comprises applying to the said article a condensate of (1) a dicarboxylic acid with (2) a mixture of (a) a diaminopolyalkyleneoxy compound and (b) an aliphatic, cycloaliphatic or aromatic diamine as hereinafter defined or an aliphatic, cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam as hereinafter defined or a mixture of the said diamine and amino acid or lactam.

Instead of a single dicarboxylic acid, diaminopolyalkylenenoxy compound, amino acid or lactam, or diamine mixture of the said compounds may be used.

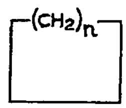
The condensates used in the process of our invention may conveniently be obtained by mixing the components and heating them, for example at a temperature within the range 150°C. to 300°C. for from 30 minutes to 5 hours. In preparing the condensates there may be used instead of the dicarboxylic acids themselves certain derivatives of the dicarboxylic acids which give rise to the same condensates, for example the esters especially the lower alkyl esters, and the halides of the said acids. The preparation of certain of the condensates is described more fully in our copending Applications Nos. 10769/65, 32449/64 and 10768/65 (Serial Nos. 1108812)

The dicarboxylic acids used in preparing the condensates are preferably aliphatic dicarboxylic acids of the formula—

$$HO_2C.[CH_2]_nCO_2H$$

in which n represents zero or a positive integer from 1 to 10. Adipic acid is particularly suitable. Other suitable aliphatic dicarboxylic acids include oxalic acid, succinic acid, glutaric acid, sebacic acid and dodecanedioc acid.

Other suitable dicarboxylic acids are cycloaliphatic, alkylcycloaliphatic, aromatic and alkyl aromatic dicarboxylic acids. By cycloaliphatic dicarboxylic acids we mean acids containing an alkylene ring structure represented by the formula—



wherein n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by two carboxy groups to form the corresponding dicarboxylic acids. If aromatic acids are used the carboxylic groups should not lie on adjacent carbon atoms of a ring system. Examples of such dicarboxylic acids include hexahydroterephthalic acid, hexahydro - p - xylylenedicar - boxylic acid, p-xylylenedicarboxylic acid, terephthalic acid and isophthalic acid.

The diaminopolyalkyleneoxy compounds used in preparing the condensates are linear compounds containing two terminal amino groups joined directly or through suitable linking groups to a polyalkylenenoxy chain. Such compounds may conveniently be represented by the formula—

$$NH_2.X[\text{alkylene } O]_nY\ NH_2$$

in which X represents a direct link or a linking group, Y represents a linking group and n is a positive integer which is at least 2 and preferably at least 7. The alkylene groups in any one polyalkyleneoxy chain may be all the same or the chain may contain more than one kind of alkylene group, for example it may contain a mixture of ethylene and propylene group. The alkylene groups may contain from 2 to 12 carbon atoms but ethylene groups are particularly preferred. Such diaminopolyalkyleneoxy compounds may be obtained, for example, from a polyalkyleneoxydiol of the formula—

$$HO[\text{alkylene } O]_{n+1}\ H$$

by conversion of the hydroxyl groups into halogen atoms, for example into chlorine atoms by reaction with thionyl chloride, followed by reaction of the resulting dihalogeno compound with ammonia to give the corresponding diamino compound; in which case X represents a direct link and Y represents an alkylene group. Alternatively they may be obtained from a polyalkyleneoxydiol of the formula—

$$HO[\text{alkylene } O]_nH$$

by reaction with acrylonitrile to give the bis-β-cyanoethyl ether followed by reduction to the corresponding bis-γ-aminopropyl ether; in which case X represents the group

$$—CH_2CH_2CH_2O—$$

and Y represents the group

$$—CH_2CH_2CH_2—.$$

Alternatively again they may be obtained from a polyalkylene-oxydiol of the formula—

$$HO[\text{alkylene } O]_nH$$

by reacting with a 2-aminomethyl-3,4-dihydro-2H-pyran as described in our copending Application No. 5173/65; (Serial No. 1087335) in which case X represents a 2-methylenetetrahydropyran-6-yloxy group and Y represents a 2-methylenetetrahydropyran-6-yl group.

The diaminopolyalkyleneoxy compounds also include those diamines which may be prepared in known manner from alkylene oxide condensates containing two hydroxyl groups. Such alkylene oxide condensates may be obtained by reacting an alkylene oxide or a mixture of alkylene oxides with a compound containing two hydrogen atoms reactive with the alkylene oxide, for example water, a diol, a dihydric phenol, a dicarboxylic acid, a primary amine, a primary amide or a bis-secondary amine. Such alkylene oxide condensates include—

(1) alkylene oxide condensates of glycols, especially of glycols containing more than 4 carbon atoms, for example 1,6-hexanediol,

(2) alkylene oxide condensates of primary amines for example methylamine, ethylamine and hexadecylamine, and

(3) alkylene oxide condensates of dihydric phenols, for example diphenylol propane.

Particularly preferred alkylene oxides are ethylene oxide and propylene oxide, although other alkylene oxides such as 1,2- and 2,3-butylene oxides may be used. Conversion of the alkylene oxide condensates containing two hydroxyl groups into the diaminopolyalkyleneoxy compounds may be effected, for example, by the methods already described for conversion of polyoxyalkylenediols into diaminopolyalkyleneoxy compounds. The diaminopolyalkyleneoxy compounds preferably have a molecular weight within the range 300 to 6000.

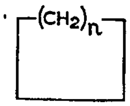
The aliphatic, cycloaliphatic or aromatic diamines used in preparing the condensates may be any aliphatic, cycloaliphatic or aromatic diamines, including alkyl cycloaliphatic and alkyl aromatic diamines, provided that where the two amino groups are attached to a ring of carbon atoms they are not attached to the same carbon atom or to adjacent carbon atoms therein. Particularly preferred, however, are aliphatic diamines having the formula—

$$NH_2.[CH_2]_n\ NH_2$$

in which n represents a positive integer of from 2 to 12. Hexamethylene diamine is particularly suitable. Other suitable aliphatic diamines include ethylene diamine, nonamethylene diamine, decamethylene diamine, dodeca-

methylene diamine and β-methylhexamethylene diamine.

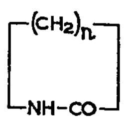
As cycloaliphatic diamines we prefer to use diamines containing an alkylene ring structure—



wherein n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by two amino groups to form the corresponding diamines. Examples of suitable cycloaliphatic and aromatic diamines are 1,3- and 1,4-diaminocyclohexane, p-xylene diamine, p-phenylene diamine and p-tolylene diamine. The diamine may be used in the form of a salt with the dicarboxylic acid.

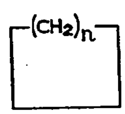
By aliphatic amino acids or lactams we mean in particular ω-amino aliphatic carboxylic acids and the derived lactams. Particular compounds of this class may be represented by one of the formulae—

$$NH_2[CH_2]_nCO_2H \quad \text{or}$$



in which n is a positive integer from 5 to 11. Caprolactam is particularly suitable. Other suitable lactams include laurinolactam (dodecanolactam), enantholactam and capryllactam.

The cycloaliphatic amino acids used may be any such amino acids provided that the amino group and the carboxyl group are not attached to the same carbon atom or to adjacent carbon atoms in the ring. We prefer, however, to use amino acids containing an alkylene ring structure represented by the formula—



where n is from 5 to 16, two hydrogen atoms not on the same or adjacent carbon atoms being replaced by an amino and a carboxyl group respectively.

In alkyl cycloaliphatic amino acids the amino and carboxyl groups can be attached to the ring or to side chain carbon atoms.

Examples of cycloaliphatic and alkyl cycloaliphatic amino acids include 4-aminocyclohexanecarboxylic acid, 4-aminomethylcyclohexanecarboxylic acid and 4-aminocyclohexylacetic acid.

It is preferred to use those condensates where the amount of dicarboxylic acid used in the preparation is the approximate stoichiometric equivalent of the amounts of diamine used, by which is meant the sum of the amount of diaminopolyalkyleneoxy compound and aliphatic, cycloaliphatic or aromatic diamine. It is also preferred that the ratio of the weight of the diaminopolyalkyleneoxy compound to the combined weight of aliphatic, cycloaliphatic or aromatic diamine and aliphatic, cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam should lie within the range 10:90 to 95:5.

The condensates are usually solids, often of a rubbery nature. Depending on the amount of diaminopolyalkyleneoxy compound used they show varying degrees of solubility in water, the solubility increasing with the proportion of alkyleneoxy groups in the molecule. Those compounds which are not soluble in water are readily dispersible in aqueous media.

Natural polymeric material which may be treated includes cellulosic material and proteinaceous material such as keratin. Synthetic polymeric material which may be treated includes polyolefines, such as polyethylene and polypropylene, polyamides such as nylon, including polymers of caprolactam, polyesters such as polyethylene terephthalate, polymers and copolymers of acrylonitrile, cellulose esters such as cellulose triacetate and glass.

The shaped articles may be of any desired kind. They may be obtained from the polymeric material by any known shaping process for example by casting, moulding or extrusion. The process of our invention is particularly applicable, however, to filaments, fibres, foils and films and especially to textile materials comprising such filaments or fibres. Textile materials include rovings, yarns, non-woven webs and woven and knitted fabrics as well as filaments and fibres. Natural polymeric material may already be in fibrous form, as for example cotton and wool fibres, or may be converted into fibrous form as for example in the conversion of natural cellulose into the cellulosic rayons. Synthetic polymeric material may be converted into fibrous form by wet or dry spinning operations as may be appropriate.

The process of the invention may be used for example to treat cellulosic textile materials in order to modify the handle or improve the abrasion resistance. The process may also be used on cellulosic textile materials in conjunction with a crease-resisting agent such as a resin in order to impart a crease resist effect which is greater than that obtained with the crease resisting agent alone.

The process is particularly suitable for the

treatment of shaped articles, especially textile materials and films, composed of hydrophobic synthetic polymeric material.

It is well known that shaped articles made from hydrophobic polymeric material besides having a very limited capacity for absorbing moisture become electrified readily when subjected to friction. These properties are disadvantageous in that the electrified articles readily attract dirt and dust. Moreover film composed of hydrophobic polymeric material which has become electrified is difficult to handle in that it becomes attracted to and clings to other articles. Further, textile materials composed of hydrophobic polymeric material which are used for clothing, besides having the disadvantage of soiling readily, tend to be uncomfortable in wear owing to the limited capacity for absorbing moisture. Such materials include those composed of polyolefines, polyamides, polyesters, polymers and copolymers of acrylonitrile and cellulose triacetate.

Since the condensates are readily dispersible in water, and may be soluble in water, it is convenient to apply them to the shaped articles from an aqueous medium. If desired, however, a solution or dispersion in an organic solvent or in a mixture of an organic solvent with water may be used. The solution or dispersion may be applied to the shaped article by any suitable method, for example by dipping, impregnation or spraying, or by application with a brush, furnishing roller or squeegee. The application conveniently takes place at the ordinary temperature but if desired may take place at a moderately elevated temperature for example at temperatures up to 50°C.

After application of the solution or dispersion the shaped article may be dried, if desired at the ordinary temperature, but conveniently at elevated temperatures up to about 120°C.

The amount of the condensation product applied to the shaped article may be varied within wide limits. In most cases, however, the amount applied lies within the range 0.1% to 5% of the weight of the shaped article.

In some cases it may be convenient to bake the shaped article after application of the condensation product so as to improve its fixation. For example the shaped article may be heated at a temperature within the range 120°C. to 220°C. for from 10 seconds to 30 minutes.

There may also advantageously be applied to the shaped article, in addition to the condensation product, a crosslinking agent or a resin precondensate and if desired a catalyst, which will react with the condensation product and assist in fixing the latter on the shaped article for example by reducing its solubility in water. Such materials may be applied together with the condensation product or by they may be applied as a separate step, but their application should normally precede the baking treatment where such is used.

Suitable cross linking agents include aldehydes and dialdehydes such as formaldehyde, acrolein and glyoxal, capable of crosslinking reactions; and cyanuric halides and dihalogenotriazine derivatives. Resin precondensates include the initial stage condensation products of formaldehyde with nitrogen compounds such as urea, thiourea, dicyandiamide, amides, amines, carbamates, aminotriazines, urons, ureins, ureides, imidazolidones, pyridones and triazones, especially the methylol derivatives of such compounds and the lower alkyl ethers of such methylol derivatives; the methylol derivatives of nitrogen containing polymers such as water-soluble urea/formaldehyde polycondensates, polyacrylamide and addition copolymers containing acrylamide, and the lower alkyl ethers of such methylol derivatives; and polyacetals such as the acetal condensation products of aldehydes such as formaldehyde, acetaldehyde, glyoxal, malondialdehyde, succindialdehyde, adipaldehyde, hydroxyadipaldehyde and terephthalaldehyde with alcohols such as ethylene glycol, diethylene glycol, glycerol, pentaerythritol and dipentaerythritol, especially polyacetals of the type described in US Patent Specifications 2,785,947; 2,785,948; 2,785,949, 2,785,995; 2,785,996 and 2,786,081.

If a catalyst is used it should be chosen so as to promote the reaction of the resin precondensate with itself or of the resin precondensate or cross-linking agent with the condensation product or with the shaped article or with both.

The catalyst may, for example, be an acid or an alkaline catalyst. In the case of resin precondensates, weakly acid substances or substances which liberate acid on heating are particularly suitable. As examples of such substances there may be mentioned, amongst others, organic acids such as oxalic acid; salts of weak bases and strong acids such as zinc chloride, the mineral acid salts of organic amines and especially ammonium salts such as ammonium sulphate and ammonium chloride; and substantially neutral substances which develop acidity on heating such as magnesium chloride and ammonium thiocyanate. Mixtures of such catalysts may be used if desired.

There may also be applied to the shaped article in conjunction with the condensation products other compounds which may serve to modify or enhance the effect achieved by the condensation product alone. Such compounds include, for example, hydroxyalkyl ethers of cellulose or starch.

There may also be applied to the shaped article in conjunction with the condensation

products antioxidants or stabilisers which serve to prevent decomposition of the condensation products, especially where the process includes a high temperature baking treatment.

By an antioxidant we mean a compound which prevents or retards the oxidation of organic compounds. Suitable antioxidants are those compounds which are already known as antioxidants for use in foodstuffs, in natural and synthetic rubbers, in lubricating oils and in polymers such as the polyolefines. Many compounds of this kind are already well known in the art. Among numerous publications in which such compounds are described there may be mentioned 'Autoxydation, Mesures de Prévention, Antioxydants' by M. Vigneron and 'Rubber Chemicals' by J. van Alphen (Elsevier Publishing Company, 1956).

Particularly suitable for use as antioxidants in the process of our invention are compounds of the following classes—

(i) polyhydric phenols such as pyrogallol, and esters of gallic acid;
(ii) substituted monohydric phenols, particularly alkylcycloalkyl-, aralkyl-, aryl-, and alkoxy- substituted phenols for example 2-(α-methylcyclohexyl)-4,6-dimethylphenol; 2,6-di-*t*-butyl-4-methylphenol; 4-benzyl-2,6-dihydroxymethylphenol and 2,6-di-*t*-butyl-4-methoxyphenol;
(iii) bis-phenols such as bis-(2-hydroxy-3-(α - methylcyclohexyl) - 5 - methyl - phenyl)methane, 1,1-bis-(2-hydroxy-3,5-dimethylphenyl)-n-nonane and bis-(3 - *t* - butyl - 2 - hydroxy - 5 - methylphenyl)methane;
(iv) sulphides such as dilaurylthiodipropionate, dioctylsulphide and bis-(5-*t*-butyl - 4 - hydroxy - 2 - methyl - phenyl) sulphide;
(v) dithiocarbamates such as sodium diethyldithiocarbamate, zinc diethyldithiocarbamate, zinc dinonyldithiocarbamate, 2,6 - bis - (piperidinothio - carbonylthiomethyl) - 4 - methyl - phenol and 2,6-di-*t*-butyl-4-diethylthiocarbamoylthiomethylphenol;
(vi) dialkyldithiophosphates such as zinc dinonyldithiophosphate.

After the application of the condensation product to the shaped article, and, if desired, the baking treatment, the shaped article may be rinsed in water and, if desired, washed in a hot solution of a detergent which may also contain an alkali, such as soda ash to neutralise any residual acidic catalyst. Finally, the shaped article may be rinsed with water and dried.

Where the shaped article is a textile material the process of the invention may be applied before, in conjunction with, or after other chemical or mechanical finishing operations such as those used to confer resistance to shrinkage and creasing, modification of handle or surface lustre, water-repellency and optical brightness.

Shaped articles treated according to the present process are altered very little in appearance and retain their desirable characteristics. Textile materials composed of hydrophobic polymeric material retain their inherent characteristics, such as resistance to creasing or crushing, but usually they feel fuller and warmer to the touch. Their moisture absorbency is improved as a result of the treatment and their tendency to become electrified and to soil is diminished. These desirable properties are not easily destroyed by repeated washing and cleaning operations.

The invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight—

Example 1

70 Parts of α,ω-diaminopolyoxyethylene of mol.wt. 1460, 30 parts of the salt of hexamethylene diamine and adipic acid, 7 parts of adipic acid and 100 parts of water were heated in a sealed vessel to 220°C. for $\frac{3}{4}$ hour. The pressure was then released over $\frac{1}{2}$ hour and the temperature simultaneously raised to 270°C. The temperature was held at 265—270°C. under a stream of nitrogen for two hours. The product was cooled and crushed.

A piece of synthetic polyamide continuous filament fabric was impregnated with an aqueous solution containing 5 parts of a 10% solution of the above product in 50:50 aqueous ethanol, and 95 parts of water. The fabric was then squeezed so as to retain 50% of its dry weight of liquor, and dried at 100° C.

The resulting fabric, compared to an untreated control fabric, had a reduced tendency to require charges of static electricity and possessed improved moisture absorbency.

Example 2

A piece of a synthetic polyamide continuous filament fabric was impregnated with an aqueous solution containing 5 parts of a 10% solution of the product prepared as described in Example 1 in 50:50 aqueous ethanol, 0.4 part of a urea/formaldehyde condensate prepared as described in Example 2 of British Patent Specification No. 953,754, 0.2 part of ammonium chloride and 94.4 parts of water. The fabric was then squeezed so as to retain 50% of its dry weight of liquor, dried at 120°C. and baked at 150°C. for 3 minutes.

The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and possessed improved moisture absorbency. These effects were maintained after repeated washing.

Example 3

A piece of a synthetic polyamide continuous filament fabric was impregnated with an aqueous solution containing 5 parts of a 10% solution of the condensation product of α,ω-diaminopolyoxymethylene of mol.wt. 1464, caprolactam and adipic acid prepared as described in Example 3 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65 (Serial Nos. 1108812) in 50:50 aqueous ethanol, and 95 parts of water. The fabric was then squeezed so as to retain 50% of its dry weight of liquor, and dried at 100°C.

The resulting fabric, compared to an untreated control fabric, had a reduced tendency to acquire charges of static electricity and possessed improved moisture absorbency.

Example 4

A piece of a synthetic polyamide continuous filament fabric was impregnated with an aqueous solution containing 5 parts of a 10% solution of the condensation product of α,ω-diaminopolyoxyethylene of mol.wt.1464, caprolactam and adipic acid prepared as described in Example 4 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65 Serial No. 1108812 in 50:50 aqueous ethanol, 0.4 part of a urea/formaldehyde condensate prepared as described in Example 2 of British Patent Specification No. 953,754, 0.2 part of ammonium chloride and 94.4 parts of water. The fabric was then squeezed so as to retain 50% of its dry weight of liquor, dried at 120°C. and baked at 150°C. for 3 minutes.

The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and improved moisture absorbency.

These effects were maintained after repeated washing.

Example 5

A piece of a synthetic polyamide continuous filament fibre fabric was treated as described in Example 4 with an aqueous solution containing 1.5 parts of a hydroxyethylated cellulose, 5 parts of a 10% solution of the condensation product of α,ω-diaminopolyoxyethylene of mol.wt.1464, caprolactam and adipic acid prepared as described in Example 4 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65 (Serial Nos. 1108812) in 50:50 aqueous ethanol, 0.4 part of an etherified polymethylol melamine/urea precondensate as described in Example 10 of British Patent Specification No. 953,754, 0.2 part of ammonium chloride and 92.9 parts of water.

After washing at 50°C. for 5 minutes in a solution containing 0.1% of a non-ionic detergent and 0.1% soda ash to remove any unreacted material, the fabric was rinsed with water and dried.

The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity, improved moisture absorbency, and a reduced tendency to soil.

These effects were maintained after repeated washing.

Example 6

A piece of a polyacrylonitrile fibre fabric was impregnated with an aqueous composition containing 50 parts of a 10% solution of the condensation product of α,ω-diaminopolyoxyethylene of mol.wt.1464, caprolactam and adipic acid prepared as described in Example 4 of the complete specification filed in our copending Applications Nos. 10769/65, 32449/64 and 10768/65 Serial No. 1108812 in 50:50 aqueous isopropanol, 1 part of a 20% non-ionic aqueous dispersion of the antioxidant, bis - (2 - hydroxy - 3 - (α - methyl - cyclohexyl)-5-methylphenyl) methane, and 49 parts of water. The fabric was squeezed so as to retain 40% of its dry weight of liquor, dried at 120°C. for 1 minute and baked at 135°C. for 3 minutes.

The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire electrostatic charges, both before and after washing.

Example 7

A piece of a polyester fibre fabric was impregnated with an aqueous composition containing 50 parts of a 10% solution of the condensation product of α,ω-diaminopolyoxyethylene of molecular weight 1464, caprolactam and adipic acid prepared as described in Example 4 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65 (Serial No. 1108812) in 50:50 aqueous isopropanol and 1 part of a 20% aqueous non-ionic dispersion of the antioxidant, bis-(2-hydroxy-3-(α - methylcyclohexyl) - 5 - methylphenyl) - methane, and 49 parts of water. The polyester fabric was then squeezed so as to retain 20% of its dry weight of liquor, dried at 110°C. for 1 minute and subsequently heated at 180°C. for 30 seconds.

The treated fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire electrostatic charges and to be soiled by greasy dirt.

Example 8

60 Parts of α,ω-diaminopolyoxyethylene of mol.wt. 1540, 40 parts of caprolactam and 5.7 parts of adipic acid are stirred together at 250°C. under a stream of oxygen-free nitrogen for 2 hours. The product is discharged into a well-stirred mixture of 900 parts of water and 400 parts of isopropanol,

previously heated to 60°C. A clear solution is obtained, setting to a gel on cooling.

A piece of a polyamide continuous filament fabric was impregnated with an aqueous solution prepared by adding 36 parts of the above solution, 0.4 part of a urea/formaldehyde condensate prepared as described in Example 2 of British Patent Specification No. 953754 and 0.2 part of ammonium chloride to 63.6 parts of water. The fabric was then squeezed so as to retain 50% of its dry weight of liquor, dried for 1 minute at 120°C. and baked for 1 minute at 160°C. The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and improved moisture absorbency. These effects were maintained after repeated washing.

Example 9

25 Parts of an aminomethyltetrahydropyranyl-terminated polyoxyethylene (prepared from polyoxyethylene glycol of molecular weight 1540 by reaction with aminomethyl dihydropyran), 25 parts of caprolactam and 2.6 parts of adipic acid are reacted together at 190°C. under a stream of oxygen-free nitrogen for 3½ hours, and then at 190°C./15 mm. pressure for 1¼ hours to give a hard, somewhat brittle polymer.

30 Parts of the polymer are dissolved in a mixture of 120 parts of water and 120 parts of isopropanol.

A piece of a polyamide continuous filament fabric was impregnated with an aqueous solution prepared by adding 14.4 parts of the above solution, 0.4 part of a urea/formaldehyde condensate prepared as described in Example 2 of British Patent Specification No. 953754 and 0.2 part of ammonium chloride to 85 parts of water. The fabric was then squeezed so as to retain 50% of its dry weight of liquor, dried for 1 minute at 120°C. and baked for 1 minute at 160°C. The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and improved moisture absorbency. These effects were maintained after repeated washing.

Example 10

A piece of a polyethylene terephthalic fibre fabric was impregnated with an aqueous composition containing 80 parts of a 10% solution of the product prepared as described in Example 1 in 50:50 aqueous isopropanol, 1.6 parts of a urea/formaldehyde condensate prepared as described in Example 2 of British Patent Specification No. 953754, 0.8 part of ammonium chloride, 1 part of a 20% aqueous non-ionic dispersion of the antioxidant, bis-(2 - hydroxy - 3 - (α - methylcyclohexyl) - 5 - methylphenyl)methane, and 16.6 parts of water. The fabric was squeezed so as to retain 25% of its dry weight of liquor, dried at 110°C. for 1 minute and then heated at 140°C. for a further minute.

The resulting fabric, compared to an untreated polyethylene terephthalate fabric, possessed a reduced tendency to acquire electrostatic charges and was also more water absorbent. These effects were retained after repeated laundering.

Example 11

A piece of a polyacrylonitrile fibre fabric was impregnated with an aqueous composition containing 50 parts of a 10% solution of the product prepared as described in Example 1 in 50:50 aqueous isopropanol and 0.6 part of a 20% aqueous non-ionic dispersion of the antioxidant, bis-(2-hydroxy-3-(α-methylcyclohexyl)-5-methylphenyl)methane, and 49.4 parts of water. The fabric was squeezed so as retain 40% of its dry weight of liquor, dried at 120°C. for 1 minute and then heated at 140°C. for 3 minutes.

The treated fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and to pick up greasy soil.

Example 12

A piece of a polyamide fibre fabric was impregnated with an aqueous composition containing 66 parts of a 10% solution of the product prepared as described in Example 1 in 50:50 aqueous ethanol, 0.8 part of a 20% aqueous non-ionic dispersion of the antioxidant, bis - (2 - hydroxy - 3 - (α - methyl - cyclohexyl) - 5 - methylphenyl)methane, and 33.2 parts of water. The fabric was squeezed so as to retain 30% of its dry weight of liquor, dried at 110°C. for 1 minute and heated at 140°C. for a further minute.

The resulting fabric, compared to an untreated control fabric, possessed not only a reduced tendency to acquire electrostatic charges but also improved moisture absorbency. These properties were permanent to repeated mild laundering.

Example 13

A piece of a cellulose triacetate fibre fabric was impregnated with an aqueous composition containing 17 parts of a 10% solution of the condensation product of α,ω-diaminopolyoxyethylene of molecular weight 1464, caprolactam and adipic acid prepared as described in Example 4 of the complete specification filed in our copending Applications Nos. 10769/65, 32449/64 and 10768/65 (Serial No. 1108812) in 50:50 aqueous isopropanol, 0.5 part of a 20% aqueous non-ionic dispersion of the antioxidant, bis-(2-hydroxy-3-(α-methylcyclohexyl) - 5 - methylphenyl)methane, and 82.5 parts of water. The fabric was squeezed so as to retain 60% of its dry weight of liquor, dried at 60°C. for 10 minutes and then heated at 180°C. for 30 seconds.

The treated fabric possessed a reduced tendency to acquire electrostatic charges and a greater resistance to contamination by grease compared to an untreated control fabric.

EXAMPLE 14

A cotton poplin fabric was impregnated with a composition containing 16 parts of a 50% aqueous solution of dimethyl ethylene urea, 12 parts of 10.5% aqueous dispersion of the condensation product of α,ω-diaminopolyoxyethylene of molecular weight 1532, caprolactam, hexamethylene diamine and adipic acid prepared as described in Example 6 of the complete specification filed in our copending Applications Nos. 10769/65, 32449/64 and 10768/65, Serial No. 1108812 0.8 part of zinc nitrate hexahydrate and 71.2 parts of water. The fabric was squeezed so as to retain 50% of its dry weight of liquor, dried at 110°C. for 1 minute and then baked at 150°C. for 3 minutes. It was washed off in a solution containing 0.1% of a non-ionic detergent for 5 minutes at 50°C.

The treated cotton possessed superior high speed stitching performance and improved abrasion resistance compared to the cotton fabric treated with dimethyl ethylene urea in the absence of the condensation product of α,ω - diaminopolyoxyethylene, caprolactam, hexamethylene diamine and adipic acid.

EXAMPLE 15

A piece of a polyamide fibre fabric was impregnated with a composition containing 27 parts of a 12.5% aqueous dispersion of a condensation product of α,ω-diaminopolyoxyethylene of molecular weight 1532, caprolactam and dimethyl terephthalate prepared as described in Example 12 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65, (Serial No. 1108812) 0.7 part of the methylated urea-formaldehyde condensate prepared as described in Example 8 of British Patent Specification No. 953,754, 0.3 part of ammonium chloride, 0.8 part of a 20% non-ionic dispersion of the antioxidant bis-(2-hydroxy-3 - (α - methylcyclohexyl) - 5 - methyl - phenyl)methane, and 71.2 parts of water. The fabric was squeezed so as to retain 30% of its dry weight of liquor and then dried by heating at 150°C. for 1 minute. The resulting fabric, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and much improved water absorbency. These effects were retained after washing.

EXAMPLE 16

A piece of a polyamide fibre fabric was impregnated with a composition containing 25 parts of a 12.5% aqueous dispersion of the condensation product of α,ω-diaminopolyoxyethylene of molecular weight 1532, caprolactam and dimethyl terephthlate prepared as described in Example 12 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65, Serial No. 1108812 1 part of sodium 1-dichlorotriazinylaminonaphthalene - 5 - sulphonate, 2 parts of sodium bicarbonate and 72 parts of water. The fabric was squeezed so as to retain 50% of its dry weight of liquor, dried at 60°C. for 5 minutes and then heated at 180°C. for 30 seconds. The treated nylon possessed superior moisture absorbency and anti-static performance to the untreated fabric, both before and after washing.

EXAMPLE 17

A piece of a polyamide fibre fabric was impregnated with a composition containing 34 parts of a 9.3% solution in 50:50 aqueous isopropanol of the condensation product of the diamine prepared by reacting a condensate of octadecylamine and 18 moles of ethylene oxide successively with thionyl chloride and ammonia, caprolactam and adipic acid made as described in Example 13 of the complete specification filed on our copending Applications Nos. 10769/65, 32449/64 and 10768/65 (Serial No. 1108812), 0.7 part of the methylated urea-formaldehyde condensate prepared as described in Example 8 of British Patent Specification No. 953754, 0.3 part of ammonium chloride, 0.8 part of a 20% non-ionic dispersion of the antioxidant, bis-(2-hydroxy - 3 - (α - methylcyclohexyl) - 5 - methylphenyl)methane, and 64.2 parts of water. The fabric was squeezed so as to retain 30% of its dry weight of liquor and dried by heating at 150°C. for 1 minute.

The treated nylon, compared to an untreated control fabric, possessed a reduced tendency to acquire charges of static electricity and improved water absorbency, both before and after laundering.

WHAT WE CLAIM IS:—

1. A process for the treatment of shaped articles composed of natural or synthetic polymeric material which comprises applying to the said article a condensate of (1) a dicarboxylic acid with (2) a mixture of (a) a diaminopolyalkyleneoxy compound and (b) an aliphatic, cycloaliphatic or aromatic diamine as hereinbefore defined or an aliphatic, cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam as hereinbefore defined or a mixture of the said diamine and amino acid or lactam.

2. A process as claimed in claim 1 in which the dicarboxylic acid component of the condensate is an aliphatic dicarboxylic acid of the formula—

$$HO_2C[CH_2]_n\ CO_2H$$

in which n represents zero or a positive integer from 1 to 10.

3. A process as claimed in either or claims 1 or 2 in which the dicarboxylic acid com-

ponent of the condensate is adipic acid.

4. A process as claimed in any of claims 1 to 3 in which the diaminopolyalkyleneoxy component of the condensate is a compound of the formula—

$NH_2X[\text{alkylene O}]_n\ YNH_2$

in which X represents a direct link, Y represents an alkylene group and n is a positive integer which is at least 2.

5. A process as claimed in any of claims 1 to 3 in which the diaminopolyalkyleneoxy component of the condensate is a compound of the formula—

$NH_2X[\text{alkylene O}]_n\ YNH_2$

in which X represents a 2-methylenetetrahydropyran-6-yloxy group, Y represents a 2-methylenetetrahydropyran-6-yl group and n is a positive integer which is at least 2.

6. A process as claimed in any of claims 1 to 5 in which the diaminopolyalkyleneoxy component of the condensate contains a polyalkylenenoxy chain in which the alkylene groups are ethylene groups.

7. A process as claimed in any of claims 1 to 6 in which the diaminopolyalkyleneoxy component of the condensate has a molecular weight within the range 300 to 6000.

8. A process as claimed in any of claims 1 to 7 in which the condensate is obtained from an aliphatic diamine of the formula—

$NH_2[CH_2]_n\ NH_2$

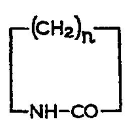
as one of the components, n representing a positive integer from 2 to 12.

9. A process as claimed in any of claims 1 to 8 in which the condensate is obtained from hexamethylene diamine as one of the components.

10. A process as claimed in any of claims 1 to 9 in which the condensate is obtained from an ω-amino aliphatic carboxylic acid of the formula—

$NH_2[CH_2]_n\ CO_2H$

or a lactam of the formula—



as one of the components, n representing a positive integer from 5 to 11.

11. A process as claimed in any of claims 1 to 10 in which the condensate is obtained from caprolactam as one of the components.

12. A process as claimed in any of claims 1 to 11 in which the condensate used is a condensate such that the amount of dicarboxylic acid used in its preparation is the approximate stoichiometric equivalent of the amount of diamine so used, that is the sum of the amount of diaminopolyalkyleneoxy compound and aliphatic, cycloaliphatic or aromatic diamine.

13. A process as claimed in any of claims 1 to 12 in which the condensate used is a condensate such that the ratio of the weight of the diaminopolyalkyleneoxy compound used in its preparation to the combined weight of aliphatic, cycloaliphatic or aromatic diamine and aliphatic cycloaliphatic or alkyl cycloaliphatic amino acid and/or lactam used lies within the range 10:90 to 95:5.

14. A process as claimed in any of claims 1 to 13 in which the shaped article is a textile material.

15. A process as claimed in any of claims 1 to 14 in which the natural polymeric material is a cellulosic material.

16. A process as claimed in any of claims 1 to 14 in which the synthetic polymeric material is a polyamide.

17. A process as claimed in any of claims 1 to 14 in which the synthetic polymeric material is a polyester.

18. A process as claimed in any of claims 1 to 14 in which the synthetic polymeric material is a polymer or copolymer of acrylonitrile.

19. A process as claimed in any of claims 1 to 14 in which the synthetic polymeric material is cellulose triacetate.

20. A process as claimed in any of claims 1 to 19 in which the amount of condensate applied to the shaped article lies within the range 0.1% to 5% of the weight of the shaped article.

21. A process as claimed in any of claims 1 to 20 in which the condensate is applied to the shaped article from an aqueous medium.

22. A process as claimed in any of claims 1 to 21 in which the shaped article is baked, after application of the condensate, at a temperature within the range 120° to 220°C. for from 10 seconds to 30 minutes.

23. A process as claimed in any of claims 1 to 21 in which there is applied to the shaped article, in addition to the condensate, a cross-linking agent or a resin precondensate and if desired a catalyst.

24. A process as claimed in claim 23 in which the cross-linking agent is a dihalogenotriazine.

25. A process as claimed in claim 23 in which the resin precondensate is an initial stage condensation product of formaldehyde with a nitrogen compound or a lower alkyl ether of a said condensation product.

26. A process as claimed in claim 25 in which a weakly acid substance or a substance which liberates acid on heating is used as a catalyst.

27. A process as claimed in any of claims 1 to 21 or 23 to 26 in which there is applied in conjunction with the condensate a hydroxyalkyl ether of cellulose or starch.

28. A process as claimed in any of claims 1 to 21 or 23 to 27 in which an antioxidant is applied in conjunction with the condensate.

29. A process as claimed in claim 28 in which the antioxidant is a bis-phenol.

30. A process as claimed in either of claims 28 or 29 in which the antioxidant is bis - (2 - hydroxy - 3 - (α - methylcyclo - hexyl)-5-methylphenyl)methane.

31. A process as claimed in any of claims 23 to 30 in which the shaped article is finally baked at a temperature within the range 120° to 220°C. for from 10 seconds to 30 minutes.

32. A process according to claim 1 for the treatment of shaped articles substantially as herein particularly described especially with reference to the Examples.

33. Shaped articles whenever treated by a process as claimed in any of claims 1 to 32.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.